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19. ABSTRACT (Continued)

## Pinned mode in polyacetylene: A distribution of soliton-lattice densities

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The *pinned* mode in optically excited polyacetylene is a vibrational envelope with a width of  $\approx 500 \text{ cm}^{-1}$  centered at  $\approx 500 \text{ cm}^{-1}$ . The width of this mode has been attributed to single solitons interacting with a wide range of pinning parameters. The constancy of the envelope for polyacetylene prepared by disparate methods (Shirakawa and Durham) and *cis-trans* ratios, casts doubt on this concept as the underlying mechanism for the shape of this vibration. The results of the work discussed here indicate that a more likely cause for the observed envelope is a superposition of spectra of various soliton lattice densities, all pinned with the same pinning mechanism.

A phenomenon which has been observed in both degenerate and nondegenerate conjugated polymers is that the production of charged defects by photoexcitation<sup>1-3</sup> induces new features in the infrared (ir) absorption spectra. Since it has been numerically demonstrated that pairs of defects (solitons) are created in optically excited polyacetylene,<sup>4</sup> these intense features are usually interpreted as vibrations localized at the defect site which derive their large oscillator strengths from very efficient coupling to the nonuniform charge in these defects. Theoretically, these intense modes have been successfully described as a linear combination of sliding modes associated with the possible structural degrees of freedom which can couple to the Raman bands in these systems.<sup>5,6</sup> Consequently, the lowest-frequency ir vibration is usually interpreted as a pinned translational or Goldstone<sup>7</sup> mode and referred to as the "pinned mode." The pinned mode in polyacetylene is an extremely broadband centered at  $\approx 500 \text{ cm}^{-1}$  with a width of  $\approx 500 \text{ cm}^{-1}$  (as compared to  $\approx 30 \text{ cm}^{-1}$  for the other observed intense ir features). The asymmetric shape, width, and location of this broadband is relatively independent of sample and/or sample preparation<sup>1,2,8</sup> as well as *cis-trans* ratio<sup>9</sup> in polyacetylene. This is in sharp contrast to the optically induced infrared absorption for nondegenerate systems such as polythiophene,<sup>3</sup> where the apparent pinned mode is of similar shape to the other intense ir features. Thus it seems very unlikely that the shape of the pinned mode in polyacetylene is due to a distribution of "pinning parameters"<sup>5,10</sup> or, equivalently, a distribution of pinning potentials which would have to be virtually independent of sample type or sample preparation.

tion.

Recent work indicates that a likely source of the pinning in these optically excited samples is the creation of equal and oppositely charged solitons on adjacent chains<sup>10,11</sup> attracting one another in a screened Coulomb potential. Consistent with this concept of pinning is not just a pair of oppositely charged solitons in a mutual Coulomb well but in general a distribution of charged-soliton concentrations in a soliton lattice configuration each of which attracts an identical but oppositely charged-soliton lattice. The pinned mode then consists of two rigid soliton lattices oscillating with respect to one another. It is the intent of this work to consider the effect of a distribution of optically excited lattices on the resultant ir absorption spectra.

For direct experimental comparison, polyacetylene has been modeled with the Su, Schrieffer, Heeger (SSH) Hamiltonian,<sup>12</sup> and for the electronic states, this has been extended to include an on-site repulsion of the Hubbard type and screened Coulomb electrostatic pinning. The electrostatic pinning results from an equal and opposite charge configuration on an adjacent chain. Since the primary concern was with the effects on the localized electronic states that occur in this problem, the Hubbard term has been considered in the mean-field unrestricted Hartree-Fock approximation. To model the vibrational modes, the SSH Hamiltonian has been extended to include multiple structural degrees of freedom in a manner analogous to that developed in the amplitude mode formalism.<sup>5</sup> As described in some detail in an earlier work<sup>10</sup> this model includes the lattice kinetic energy and couples

the  $\pi$  electrons to a set of displacement fields  $y_{a,n}$ :

$$H = - \sum_{n,\sigma} t_{n,n+1} (c_{n+1,\sigma}^\dagger c_{n,\sigma} + c_{n,\sigma}^\dagger c_{n+1,\sigma}) + \frac{1}{2} \sum_{a,n} K_a (y_{a,n+1} - y_{a,n})^2 + \frac{1}{2} \sum_{a,n} M_a \dot{y}_{a,n}^2 + \frac{U}{2} \sum_{n,\sigma} (c_{n,\sigma}^\dagger c_{n,\sigma} - \frac{1}{2}) (c_{n,-\sigma}^\dagger c_{n,-\sigma} - \frac{1}{2}) + \sum_{n,\sigma} V(n) (c_{n,\sigma}^\dagger c_{n,\sigma} - \frac{1}{2}). \quad (1)$$

In the above expression the  $c$ 's annihilate and create  $\pi$  electrons on the  $n$ th site with spin  $\sigma$ , the  $M_a$  and  $K_a$  are the effective mass and spring constant of their respective displacement fields, and  $t_{n,n+1}$  is the usual hopping integral in the SSH model. The strength of the Hubbard repulsion is  $U$ , and  $V(n)$  is the site-dependent Coulomb well. The techniques used to find the self-consistent electronic states, the resulting vibrational modes, and the subsequent ir absorption spectra are described in detail in an earlier work,<sup>10</sup> and that discussion will not be repeated here. What will be discussed in this work is the resulting ir absorption spectra obtained from considering a distribution of charge densities in a soliton lattice configuration in *trans*-polyacetylene (or equivalently a *trans*-isomer domain in material containing both *cis*- and *trans*-isomers), and the fit obtained with experimental data.

The *trans*-polyacetylene chains were modeled as rings, approximately 100 sites in circumference, with a range of charge densities from 1% to 8%. The screening in the Coulombic interaction between adjacent chains is virtually eliminated and results in a pinned frequency ( $T_1$ ) for a 1% concentration of charged solitons of  $762 \text{ cm}^{-1}$  with two additional modes ( $T_2$  and  $T_3$ ) at 1281 and  $1374 \text{ cm}^{-1}$ . By the time a charge density of 8% is reached, the resulting charge configuration is a soliton lattice with a significant amount of the charge being uniformly distributed along the chain. This results in a shallower Coulombic potential well with less curvature. Consequently, the pinned mode is substantially softened and occurs at  $83 \text{ cm}^{-1}$  with the  $T_2$  and  $T_3$  ir modes only slightly shifted to 1268 and  $1343 \text{ cm}^{-1}$ , respectively. A typical ir spectrum of chain with a fixed impurity concentration is shown in Fig. 1 for a charge density of 4%.

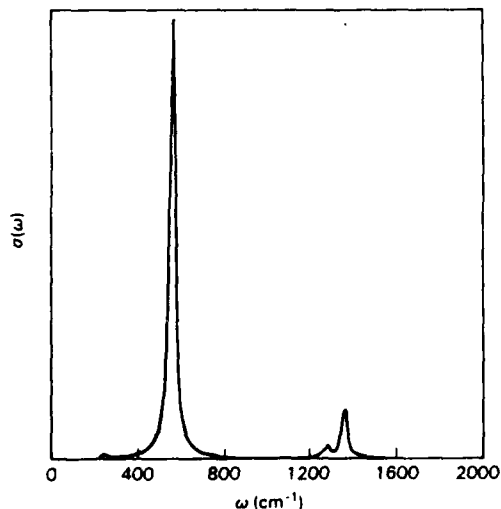


FIG. 1. Infrared absorption in optically excited  $(\text{CH})_x$  with a dopant concentration of 4%.

In Fig. 2, the frequency of the  $T_1$  and  $T_2$  mode as a function of charge concentration on the chain is shown. The significant softening of the  $T_1$  mode that occurs at large charge concentrations is more than sufficient to explain the experimental width ( $\approx 500$ )  $\text{cm}^{-1}$  of the pinned mode with the charge densities considered. Additionally, the shifts in the  $T_2$  and  $T_3$  modes, while small compared to the shift in the  $T_1$  mode, are adequate to explain the asymmetric nature of these bands.

The total calculated spectrum was obtained by interactively adding the individual spectra in order to reproduce the experimentally observed pinned mode,<sup>1,2,8,9</sup> including the low-frequency regime (down to  $\approx 100 \text{ cm}^{-1}$ ).<sup>13</sup> The resulting net spectrum and an experimental spectrum<sup>9</sup> are shown in Fig. 3. The calculated composite spectrum not only fits the pinned mode well (as it has been adjusted to do), but reproduces the asymmetrical shape of both the  $T_2$  and  $T_3$  bands remarkably well.

The relative populations of each charge concentration used to generate the total spectrum are shown in Fig. 4. These relative amounts are not unreasonable as several competing effects are operating in the sample during the excitation. For the experimental spectrum in Fig. 3, the exciting laser was an  $\text{Ar}^+$ -ion laser operating at 514 nm with an output of  $\approx 200 \text{ mW}$ . This exciting source was applied to a spot size of about 13 mm for 6 sec. From the known values of the absorption coefficient<sup>14</sup> and the crystal lattice spacing<sup>15</sup> of *trans*-polyacetylene it is straightforward to determine that over the course of the irradiation there would be nearly 800 photons incident on each

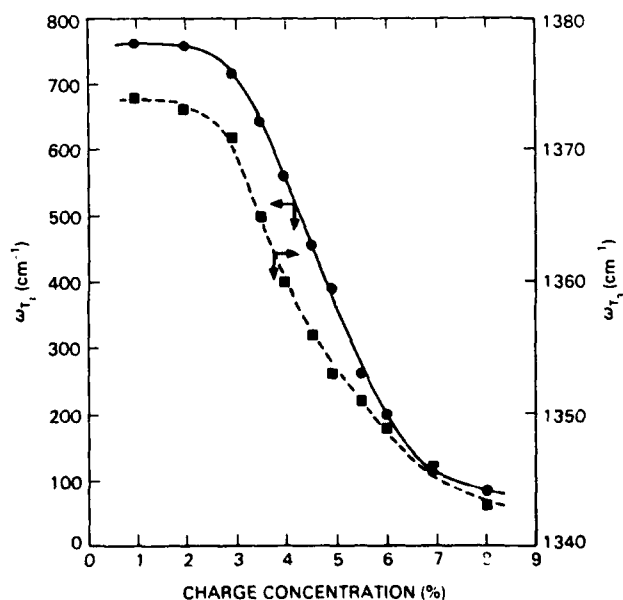


FIG. 2. Frequency of the  $T_1$  and  $T_3$  vibrational modes as a function of charge concentration.

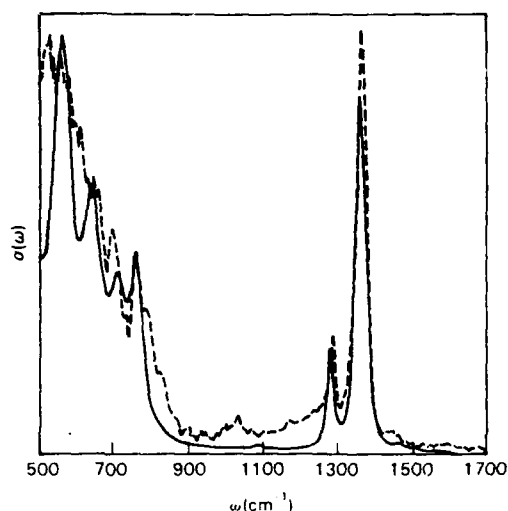


FIG. 3. Theoretical fit (solid line) of the experimental (dashed line) ir absorption spectra.

carbon site in the first molecular layer in the laser spot. Clearly it is not possible for all of these photons to result in soliton-antisoliton pairs and subsequently decay into charged solitons on separate chains. Indeed, as the soliton concentration increases the absorptivity coefficient decreases (the coefficient is calculated to decrease by nearly a factor of 10 as the soliton concentration increases from 1% to 6%). Furthermore, as the amount of separated charge increases, so too does the electrical field gradient; consequently, the separation of more charge becomes even less likely. Because of these reasons, the number of soliton-antisoliton pairs generated on chains with relatively high charge concentration is significantly reduced, and of those produced a smaller fraction are able to result in additional separated charge. Finally, those solitons which are on adjacent chains of high (but opposite) charge are much more likely to recombine than those on chains of

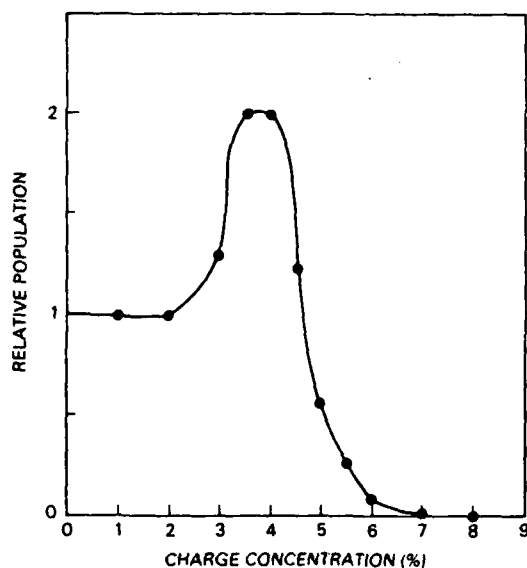


FIG. 4. Relative population of the charge concentration used to generate the theoretical ir absorption spectra shown in Fig. 3.

lower charge. Consequently, a population profile such as that of Fig. 4, wherein the maximum population is at a modest charge concentration, is not at all unreasonable.

In conclusion, there are several points to be made concerning fits with experimental ir absorption data. As already pointed out an excellent fit to the pinned mode is obtained with a very reasonable distribution of charge densities. Additionally, this concept of charges in a soliton lattice configuration, can easily account for the previously unexplained  $760\text{ cm}^{-1}$  peak at the high-frequency edge of the pinned mode, as being the pinned frequency in the low concentration or isolated region of the distribution. This band has been routinely observed whenever the spectrum is obtained using signal averaging or Fourier-transform infrared (FTIR) techniques.<sup>8,9,13</sup> There is a C-H out of plane deformation at  $740\text{ cm}^{-1}$  in the *cis*-polymer,<sup>16</sup> however, the  $760$  band does not appear to have a derivative nature,<sup>9</sup> thus, it appears to be associated with the optically excited structural defect in the polymer. The asymmetries in both the  $1290$  and  $1370\text{ cm}^{-1}$  are a natural consequence of the fit as is seen in Fig. 3. Another interesting point to be made concerns the decay of the  $T_2$  and  $T_3$  mode. Interchain charge hopping that occurs during the decay of the soliton lattice pairs will preferentially reduce the relative population of high charge densities and the  $T_2$  and  $T_3$  modes should become less asymmetric. In fact, that is what is seen experimentally<sup>9</sup> and is shown in Fig. 5. Not only is the decrease in asymmetry seen, but a slight shift to higher frequency is observed, also indicative of a decrease in the relative population of the higher concentrations. Also, note in the spectral fit in Fig. 3 the very small oscillator strengths (OS) of the  $A^{-1}$  modes at about  $1040$  and  $1440\text{ cm}^{-1}$ . This is also consistent with the experimental observation of the small OS of these modes,<sup>13</sup> which are always calculated to have much larger OS for single defects.

The optically induced infrared absorption spectra has also been obtained in nondegenerate systems.<sup>3</sup> However, unlike the degenerate systems, the lowest-frequency translational mode (the pinned mode) has approximately

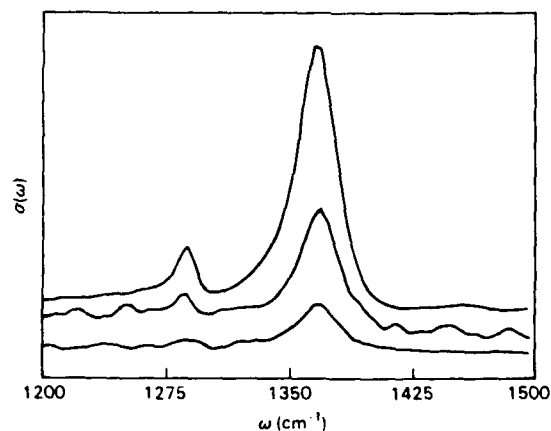


FIG. 5. Decay of the ir absorption. The first spectra is for the laser on, the second spectra is an average of 5 scans taken between 1.8 and 5.6 sec after laser is turned off, and the third spectra is an average of 40 scans taken between 1.8 and 32.3 sec after laser is turned off.

the same half-width as the other higher frequency  $T$  modes. Since it is not energetically favorable for a nondegenerate system to form a configuration which results in a significant fraction of uniform charge, it is consistent with this model that the half-width of the optically induced pinned mode would be comparable to the other  $T$  modes.

As mentioned in the Introduction, the shape of the pinned mode is independent of preparation techniques as well as *cis-trans* ratios, which argues against a distribution of pinning parameters as the correct explanation for the observed envelope. The process of interchain charge hopping for optically excited samples of  $(CH)_x$ , which leads to its observed charged defects, is most likely dependent on the microscopic environment of the polymer (crystal structure, lattice spacings, interchain  $\pi$  electron overlap, etc.), but these parameters should be relatively

independent of the method of sample preparation or *cis-trans* ratio. Thus, the explanation for the shape of the pinned mode (as well as many other observed properties in the ir spectrum) is more easily explained by assuming a distribution of charge densities in a soliton lattice configuration. Obviously a simple extension of this idea could also explain the width of the pinned mode<sup>17</sup> in chemically doped samples by assuming a microscopically nonuniform dopant distribution. This would also result in a distribution of pinning frequencies and lead to a broad absorption band for the pinned mode.

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